

Conditions for the emergence of life on the early Earth: summary and reflections

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This review attempts to situate the emergence of life on the early Earth within the scientific issues of the operational and mechanistic description of life, the conditions and constraints of prebiotic chemistry, together with bottom-up molecular fabrication and biomolecular nanofabrication and top-down miniaturization approaches to the origin of terrestrial life.

Keywords: biotic raw materials; building blocks of biomolecules; the chemical universe; complex biological matter; self-organization; structure–dynamics–function relations

1. PROLOGUE

This discussion meeting has been truly stimulating and broad in scope and content. We are particularly indebted to Dr Sydney Leach, Professor Ian Smith & Professor Charles Cockell for arranging this timely, interdisciplinary and stimulating scientific endeavour.

The ‘central dogma’ underlying this discussion meeting was that life appeared on the early Earth within 1 billion year (Gyr) of its formation. Several facets of the emergence of life (Orgel 1973; Miller & Orgel 1974; Folsome 1979; Crick 1981; Mason 1992; Lahav 1999; Deamer & Fleishaker 2005), which were discussed herein, are as follows.

- (i) The nature of biotic raw materials (Ferris 2006; Deamer 2006; Schwartz 2006; Wächtershäuser 2006).
- (ii) The origins of biotic raw materials and why and how they were present on Earth. These involve terrestrial (Bernstein 2006; Canfield 2006; Deamer 2006; Ferris 2006; Schwartz 2006) and extraterrestrial sources (Anand 2006; Grady 2006), including the ‘chemical universe’ of the interstellar medium (Thaddeus 2006).
- (iii) The constraints on prebiotic chemistry and the subsequent chemical and biochemical evolution. These include the famous presence of water (Lunine 2006), the possible role of the hot magma (Bernstein 2006), the chemical conditions (Canfield 2006; Deamer 2006; Ferris 2006; Kasting 2006), the availability of sources of energy, the prevalence of appropriate thermal conditions (Stetter 2006) and the existence of appropriate sites for biosynthesis (Cockell 2006; Deamer 2006; Ferris 2006).
- (iv) The physical and chemical conditions for the synthesis of the building blocks of biomolecules (Bernstein 2006; Ferris 2006), biomolecules (Deamer 2006; Ferris 2006) and functional biostructures (Deamer 2006).

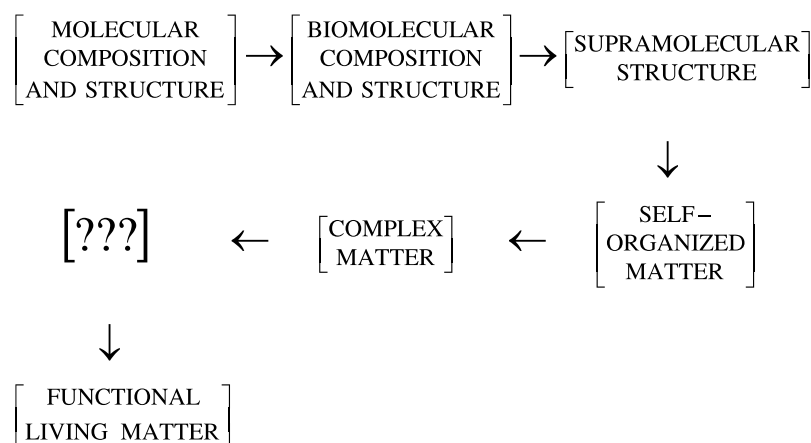
- (v) Conditions for the development of primitive life forms. These involve information recording and retrieval (Eigen 1971, 1996; Lehn 2002a,b, 2003; Deamer 2006; Ferris 2006; Taylor 2006) and energy acquisition and disposal (Canfield 2006; Kasting 2006).
- (vi) The biological conditions for further development of life on Earth. These important, exceedingly difficult and open questions address the attainment of biological complexity (Eigen 1971, 1996; Folsome 1979; Yates 1987; Lehn 2002a,b, 2003; Heckl 2004; Deamer 2006; Ferris 2006; Taylor 2006).
- (vii) The possible implications of the emergence of life on the early Earth for astrobiology. This issue addresses the transferability of the constraints and conditions of terrestrial life for the perspectives of extraterrestrial life (Chyba & Hand 2005). The exploration of Mars meteorites (Anand 2006; Grady 2006) touched on this fascinating issue.

2. WHAT IS LIFE?

Since Schrödinger (1944) asked the question, ‘What is life?’, the advancement of this provocative, scientific–intellectual challenge has acted as an inspiration to generations of scientists and scholars (Murphy & O’Neill 1995). In his famous treatise, Schrödinger (1944) inquired whether life is based on the laws of physics, because the construction and function of living matter may require a new level of description. This hypothesis was transcended by the seminal work of Crick & Watson on the structure of DNA, which established the structure–function relations in biology. Research on the primary processes in bacterial and plant photosynthesis (Deisenhofer *et al.* 1984; Feher *et al.* 1989; Michel-Beyerle 1990, 1995; Deisenhofer & Norris 1993) extended the traditional notion of the structure–function relationship. Dynamic information (in this case, the ultrafast picosecond electron transfer dynamics in the photosynthetic reaction centre) surpasses and complements

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One contribution of 19 to a Discussion Meeting Issue ‘Conditions for the emergence of life on the early Earth’.



Scheme 1.

structural information (Jortner & Bixon 1996), providing the structure–dynamics–function relations for central biological processes, which ensure life on Earth.

The description of functional living matter requires a holistic conceptual framework, with some of its cornerstones being: (i) the ideas of Onsager & Morowitz (Folsome 1979) on complex matter, (ii) the implementation of the concepts of molecular information at the molecular and supramolecular level (Eigen 1971, 1995, 1996; Yates 1987; Lehn 1988, 1990, 1995, 1999, 2000, Lehn 2002*a,b*, 2003; Eigen & Winkler 1993; Taylor 2006) and (iii) the central role of self-organization (self-assembly), which leads to the evolution of a ‘complex biological matter’ (Eigen 1971, 1995, 1996; Lehn 2002*a,b*, 2003; Heckl 2004; Deamer 2006). A heuristic, highly speculative, partial scheme for the emergence of living matter in the ‘parameter space’ of increasing complexity could be as shown in Scheme 1.

The attributes marked by [??] are unknown, being the most fascinating.

The question ‘What is life?’ is not only an extremely difficult question (Orgel 1973; Miller & Orgel 1974; Folsome 1979; Crick 1981; Lahav 1999; Deamer & Fleishaker 2005), but also perhaps not the right question (Eigen 1995; Chyba & Hand 2005). It is a popular game in this field to provide robust counter examples, which reveal failures in operational definitions (Folsome 1979; Chyba & Hand 2005). Sagan (1998) catalogues a list of failed attempts, including physiological, metabolic, biochemical, genetic and thermodynamic definitions of life, all of which face problems (Chyba & Hand 2005). For example, a metabolic definition finds it hard to exclude fire (which grows and reproduces via chemical reactions), a biochemical definition does not exclude enzymes (which are biologically functional but not living systems), while a thermodynamic definition does not exclude mineral crystals (which create and sustain local order and may reproduce). To address the question ‘What is life?’, one does not require a definition, but requires a scientific theory (Cleland & Chyba 2002, 2005). A pedagogical example (Chyba & Hand 2005) alludes to a much simpler question, ‘What is water?’, which Leonardo da Vinci (1513) faced when he attempted to characterize liquid water in terms of its phenomenological properties. This question could

only be answered in the twentieth century with the establishment of the proper molecular composition and the structure of the H₂O molecule, together with the globally condensed phase properties of the liquid, e.g. H-bonding, local order, radial and angular distribution, solvation, structure breaking, nuclear dynamics, phase transitions and response, providing a conceptual framework of an appropriate scientific theory. Regarding the conceptual framework that will provide answers to the question, ‘What is life?’, Onsager & Morowitz (Folsome 1979), Eigen (1971, 1996), Yates (1987) and Lehn (2002*a,b*, 2003), among others, made important contributions, which will start to address the significant questions regarding the emergence and function of complex biological living matter.

A notable attempt to provide a unified description of living matter was provided by the Onsager–Morowitz definition (Folsome 1979): ‘Life is that property of matter that results in the cycling of bioelements in aqueous solution, ultimately driven by radiant energy to attain maximum complexity’. This definition implies that coupled cycles involving homogeneous and/or heterogeneous chemical reactions of bioelements (i.e. prebiotic material, building blocks of biomolecules and functional biomolecular structures) in water, which are driven by the acquisition and disposal of radiant energy, result in the organization of complex matter (with ‘maximum complexity’ presumably referring to information content). Of course, there is a ubiquity of complex matter (with complexity characterized by spatial, energetic and temporal structure with variations; Kadanoff 1993) that is not alive. It appears that the Onsager–Morowitz definition bypasses the characterization of complex biological matter and how it differs from complex chemical matter. Eigen (1971, 1996) addressed the basic differences between a chemically coupled system and a living system with an abundance of chemical reactions in terms of information storage, retrieval and processing. According to Eigen (1971, 1996), all reactions in a living system follow a controlled programme operated from an information centre, whose aim is the self-reproduction of the programme itself. The three essential characteristics of all living systems yet known (Eigen 1971, 1996) are self-reproduction (without which information would be lost), mutations (which allow

evolution) and metabolism (which allows an optimal choice of a system for a certain function). Eigen (1971, 1996), Yates (1987), Lehn (2002a,b, 2003) and Heckl (2004) advanced and developed the concept of self-organization (self-assembly) and proposed that it resulted in the evolution of biological complex matter, which rests on the elements, as follows: (i) Molecular structure formation of (living and non-living) matter is driven by molecular interactions and operates on a huge diversity of possible structural combinations. (ii) Prior to the biological evolution, the chemical evolution took place, performing a selection on molecular diversity, leading to the embedment of structural information in chemical entities. (iii) The implementation of the concepts of molecular information pertains to information storage at the molecular level and the retrieval, transfer and processing of information at the supramolecular level. (iv) The formation of supramolecular structures is induced by molecular recognition (based on non-covalent intermolecular interactions, e.g. H-bonding, van der Waals interactions, charge transfer in donor–acceptor sequences and interactions in ion coordination sites). This includes self-organization, which allows adaptation and design at the supramolecular level. (v) Self-organization involves selection in addition to design at the supramolecular level, and may allow the ‘target-driven selection of the fittest’ (Lehn 2003), leading to biologically active substances.

The arsenal of self-organization of complex biological matter driven by information acquisition, storage, retrieval and transfer, which allows selection, adaptation, self-reproduction, evolution and metabolism (Eigen 1971, 1996; Yates 1987; Lehn 2002a,b, 2003), may constitute many of the missing links (marked by [???]) in scheme 1. Of course, there are many gaps in the conceptual framework for the description of complex biological matter reviewed here. In particular, the mechanistic aspects of information-driven self-organization and its implications remain to be elucidated and will be subjected to intensive and extensive experimental and theoretical scrutiny in the future. Some significant issues involve the inclusion of dissipative non-equilibrium processes in living systems (Haken 1977) and the ‘transition’ from programmed and instructed self-organized systems to ‘learning’ systems, which can be trained (Lehn 2002a,b, 2003).

3. EMERGENCE OF LIFE ON EARTH: CONDITIONS AND CONSTRAINTS

Returning to operational and mechanistic descriptions, some of the necessary prerequisites and conditions for the emergence of early life on Earth are as follows.

- (i) The existence of liquid water as a universal solvent (Darwin 1871; Oparin 1924; Blum 1962) owing to its ability for H-bonding, its function as a medium for reactivity, heterogeneous catalysis and self-organization (Bernal 1949, 1951; Ferris *et al.* 1996; Ferris 2002, 2006; Deamer 2006). Surface liquid water could become stable within 500 million years (Myr) of the Earth’s formation, i.e.

approximately 4.0 Gyr ago (Lunine 2006). Geological evidence (Watson & Harrison 2005) indicates that liquid water might have been present on Earth 4.3 Gyr ago, in contrast to the scenario of the magma oceans (Richter & Drake 1999).

- (ii) The availability of biotic raw materials (Miller & Orgel 1974; Folsome 1979; Crick 1981; Lahav 1999; Ferris 2006; Wächtershäuser 2006). These include the biotic elements (e.g. C, H, N, O, P, S, Fe, Mg, etc.), the simple biotic molecules (e.g. H₂, H₂O, NH₃, CO, CO₂, H₂S, CH₄, S and SO₂) and minerals containing Si, Fe, Ni, P and S (Deamer 2006; Ferris 2006; Schwartz 2006). Terrestrial sources of biotic raw material can be minerals (Deamer 2006; Ferris 2006; Schwartz 2006), hydrothermal sources (Whitaker & Banfield 2006; Bassez 2003; Bernstein 2006; Canfield 2006), marine aerosols (Donaldson *et al.* 2004), volcanic exhalations (Canfield 2006; Wächtershäuser 2006) and the atmosphere of primitive Earth (Miller 1953; Miller & Urey 1959; Tian *et al.* 2005). Considerable attention was devoted to biotic raw material from exogeneous sources and, in particular, to the inventory of organic molecules of extraterrestrial origin (Chyba *et al.* 1990; Thomas *et al.* 1997; Pizzarello 2004; Chyba & Hand 2005; Bernstein 2006; Cockell 2006; Thaddeus 2006). These include asteroids, meteorites and comets (Chyba *et al.* 1990; Thomas *et al.* 1997), with the Murchison meteorite (from a comet) containing a variety of organic compounds, including amino acids, purines and pyrimidines, sugar alcohols and acids (Pizzarello 2004). The exploration of the chemistry of Mars meteorites pertaining to carbon cycles on the early Earth and Mars (Grady 2006) and to Fe isotope cycles on Mars (Anand 2006) reflects a perceptive scientific approach to the open issues of Martian biological activity. Interstellar dust particles constitute another potentially important source of prebiotic raw materials (C, H and N) on Earth (Chyba & Sagan 1992; Chyba & Hand 2005; Thaddeus 2006). For some plausible, but uncertain, early atmospheric models, the cometary input of prebiotic building blocks of biomolecules, such as amino acids, may be important (Pierazzo & Chyba 1999). During the period of 4.6–3.6 Gyr ago, the organic material from comet and asteroid dust amounted to 10⁷–10⁹ kg yr^{−1}, i.e. tons per day (Bernstein 2006). It is an open question whether this dust impact has been uniform, which would have resulted in a monolayer of organic material on the surface of the Earth, or local, which would produce sites for biosynthesis.
- (iii) The availability of sources of energy, i.e. solar light, lightening, cosmic rays and heat, which induce the formation of building blocks of biomolecules (amino acids or nucleobases) from simple molecules (Miller 1953; Miller & Urey 1959; Folsome 1979; Chyba & Sagan 1992).

- (iv) The prevalence of appropriate chemical conditions. These are as follows:
 - (a) The chemical mechanisms for the production of building blocks of biomolecules (amino acids, nucleobases, phosphates, sugars and porphyrins) from simple molecules. These may rest on photochemical or radiation chemical radical reactions (Miller 1953; Miller & Urey 1959; Folsome 1979) or on a heterogeneous catalysis of the Fischer–Tropsch CO/H₂ reaction on silicon/metal oxides to form amino acids and nucleobases (Folsome 1979). The ubiquity of clay minerals was important for the following: (i) adsorption of relevant molecular species from solution (Bernal 1949, 1951) and (ii) the clay-catalysed formation of biomolecules (e.g. polypeptides, proteins and nucleobase oligomers), DNA and, in particular, RNA (Ferris *et al.* 1996; Orgel 1998*a,b*; Ferris 2002, 2006; Leman *et al.* 2004; Deamer 2006; Taylor 2006).
 - (b) The composition of the atmosphere of the early Earth (Miller 1953; Miller & Urey 1959; Stribling & Miller 1987; Tian *et al.* 2005; Canfield 2006; Kasting 2006).
 - (c) Appropriate thermal conditions, with the temperatures being sufficiently high to drive activated chemical reactions (Chyba & Hand 2005), although nuclear tunnelling can prevail at exceedingly low temperatures (Goldanskii *et al.* 1986). Concurrently, the temperatures should not be too high to ensure thermal stability, with extreme conditions prevailing for the existence of hyperthermophilic bacteria surviving up to 113°C (Stetter 2006), with this limit extending to 121°C (Kashefi & Lovely 2003).
 - (d) The existence of proper sites for biosynthesis (Cockell 2006; Ferris 2006; Deamer 2006).
- (v) Energy acquisition and disposal by functional biological systems. This could be achieved by early photosynthesis, although it is an open question whether primitive oxygenic photosynthetic organisms, which date back to 2.7 Gyr ago (Canfield 2006; Kasting 2006), preceded early forms of life such as prokaryotic cell organisms, or vice versa. This estimate is important for dating the transformation of the early Earth's atmosphere from a chemically reducing to oxidizing medium.

Energy acquisition, storage and disposal by living systems on Earth proceed in one of the two ways: by either the use of chemical energy through respiration or fermentation (involving donor–acceptor electron transfer processes) or the conversion of light energy into chemical energy. The latter process involves photosynthesis in both bacteria and plants (Deisenhofer *et al.* 1984; Feher *et al.* 1989; Michel-Beyerle 1990, 1995; Deisenhofer & Norris 1993). The two initial steps of photosynthesis involve ultrafast electronic energy transfer (time-scales of 70 fs–100 ps) in different non-universal antenna structures and ultrafast electron

transfer (time-scales of 3–200 ps) in universal arrangement of the prosthetic groups in reaction centres. The primary charge separation in photosynthetic reaction centres (figure 1), whose structure is very similar in both bacteria and plants, proceeds via a sequence of well-organized, highly efficient, directional and specific electron transfer processes between prosthetic groups across the membrane protein. Remarkable features of charge separation in both the reaction centres of bacteria and the photosystem II of plants (which allow for a quantum yield $Y \approx 1.0$ for energy conversion) on the picosecond time-scales preclude energy waste owing to energy backtransfer to the antenna and intramolecular energy damping (Bixon & Jortner 1999). Another fascinating structural feature of the reaction centres (figure 1) pertains to the two-branched membrane protein (Deisenhofer *et al.* 1984; Feher *et al.* 1989), with the prosthetic groups symmetrically arranged across the two branches, resembling a ‘Gothic window’ (figure 1). A notable feature of ultrafast picosecond electron transfer in the bacterial photosynthetic reaction centre involves structural redundancy manifested in symmetry breaking, i.e. unidirectionality of charge separation across a single ‘active’ branch of the (two-branched) membrane protein (Paddock *et al.* 2005; Poluektov *et al.* 2005). Similar features are manifested for the photosystem II of plants. This structural redundancy optimizes different functions of the end quinone groups in the ‘active’ and ‘inactive’ branches. The structural redundancy of the photosynthetic reaction centre, with the inactive branch serving as a structural element, may lead to the conjecture that the development of the early forms of photosynthetic bacteria was based on a single-branched system. The activity and composition of the ancient atmosphere in the Early Archaean period were driven by Fe-based anoxygenic photosynthesis (Canfield 2006). Geological evidence revealed the existence of anoxygenic photosynthetic organisms dating back to 3.4 Gyr ago (Westall 2006), while oxygenic photosynthetic organisms emerged approximately 2.7 Gyr ago (Canfield 2006; Kasting 2006). The nature of the (single- or double-branched) structure of the early photosynthetic organisms is an open problem.

4. THE CHEMICAL UNIVERSE

Interstellar dust particles (Leach 1996; Thaddeus 2006) might have been a source of prebiotic carbon, hydrogen and nitrogen (Chyba & Sagan 1992; Chyba & Hand 2005), perhaps pointing towards the interconnection between the interstellar chemistry and the terrestrial origin of life (Ehrenfreund *et al.* 2002).

The spectroscopic mapping of the universe by radioastronomy (Le Tueff *et al.* 2000) and optical spectroscopy (Leach 1996; Thaddeus 2006) focused on the chemical composition of both planetary atmospheres (Chyba & Hand 2005) and the interstellar medium (Leach 1996; Thaddeus 2006). These studies provided important information on the following: the cosmic abundance of the elements (Le Tueff *et al.* 2000; Thaddeus 2006); the molecules in outer space (Thaddeus 2006); and the infrared (Cook *et al.* 1996;

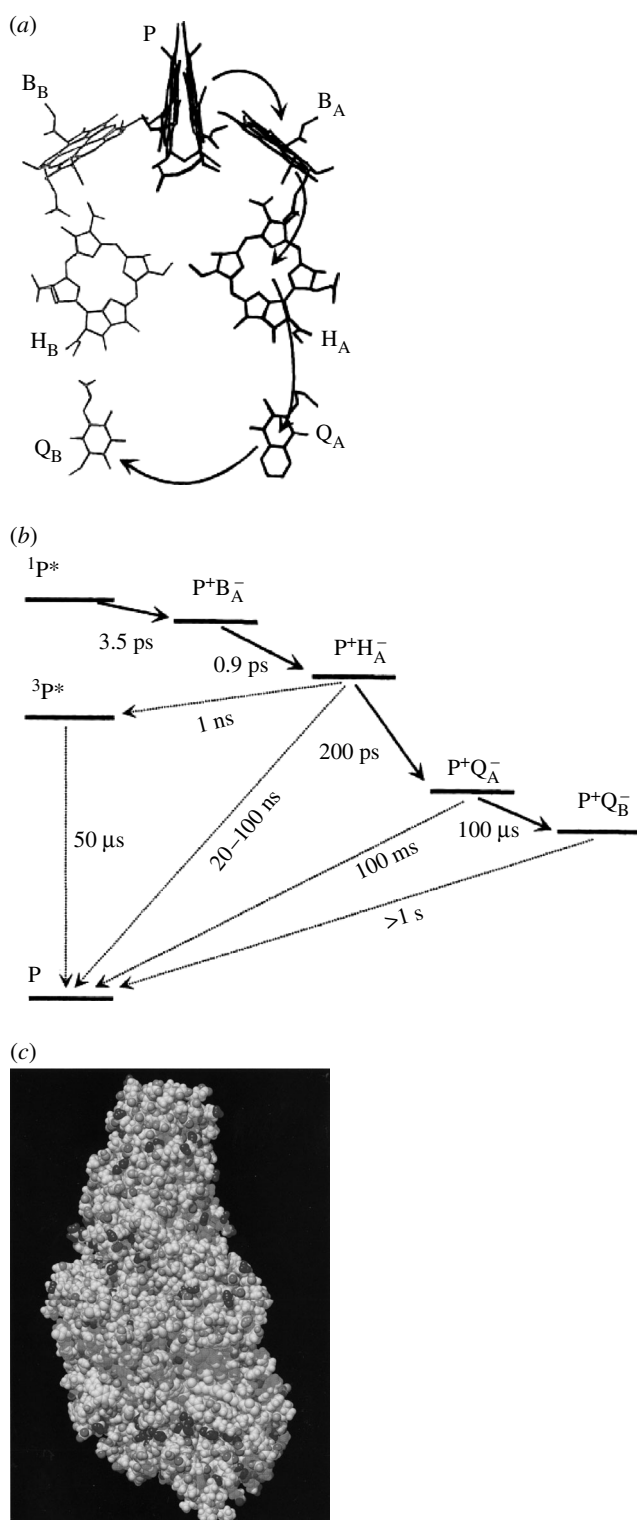


Figure 1. The bacterial photosynthetic reaction centre of *Rhodospseudomonas viridis* portraying (a) the structure (Deisenhofer *et al.* 1984) and (b) the electron transfer dynamics (Michel-Beyerle 1990, 1995; Deisenhofer & Norris 1993; Bixon & Jortner 1997). (c) The structure of the membrane protein that contains the prosthetic groups. The spatial structure of the prosthetic groups in (a) (P, bacteriochlorophyll dimer; B, accessory bacteriochlorophyll; H, bacteriopheophytin; Q, quinone) reveals two branches (labelled A and B). In (b), the kinetic scheme for charge separation with the individual rates (marked on the arrows) reveals the dominance of sequential charge separation to Q_A over the recombination processes. The structural redundancy is manifested by the exclusive charge separation across the single (A) branch.

Leach 1996; Cook & Saykally 1998; Gibb *et al.* 2000; Peeters *et al.* 2004) and visible (Herbig 1995; Snow 2001) interstellar bands that give clues to the molecular nature of interstellar dust (grains) and the elucidation of chemical reactions in outer space with the formation of cosmic dust (Leach 1996; Thaddeus 2006).

Spectroscopic studies are of considerable significance for the unambiguous identification of prebiotic single molecules and dust containing biotic raw material in the interstellar medium. These may provide biotic raw material on Earth and a molecular basis for astrobiology (Chyba & Hand 2005). From the present spectroscopic information on the interstellar molecules, the following points were inferred. (i) To date, 135 molecules were identified (Thaddeus 2006). (ii) Most of these molecules were carbon-based organic molecules (with the largest abundance of H, C and N), while molecules containing Si, P, S, Mg, Na and K were also observed (Thaddeus 2006). (iii) The largest molecule observed (Thaddeus 2006), $H-(C\equiv C)_5-CN$, contains 13 atoms (molecular weight 147). (iv) No conclusive evidence for amino acids was obtained. Recently, there has been a report (Kuan *et al.* 2003) on the detection of glycine in the interstellar medium, which created quite a stir in the astronomical community (Hollis *et al.* 2003). However, a subsequent analysis (Snyder *et al.* 2005) indicates that the spectroscopic evidence is inconclusive and the possible detection of glycine is to be taken very cautiously. (v) Interstellar grains (of approx. 1000 Å in size) constitute clusters of large organic molecules (Thaddeus 2006). Self-assembly may be operative in the 'transition' from molecules to grains. (vi) The diffuse infrared interstellar emission bands, which were assigned to C–H and C–C vibrations (Cook *et al.* 1996; Leach 1996; Cook & Saykally 1998; Peeters *et al.* 2004), are the best present evidence for the identification of dust as large structures of organic molecules. (vii) The unidentified 200–300 diffuse interstellar bands, which range from ultraviolet to near-infrared region (Herbig 1995; Leach 1996; Snow 2001; Thaddeus 2006), present an outstanding astronomical, physical, chemical and spectroscopic challenge. The electronic spectra of polycyclic aromatic hydrocarbons or their cations were considered as possible candidates (Leger *et al.* 1987; Leach 1996; Bréchnignac & Pino 1999). A recent intriguing proposal (Zhou *et al.* 2006) attributed these bands to short single-wall carbon nanotubes, e.g. $C_{160}H_{20}$, with the size distribution giving rise to the large number of bands. This proposal again points towards the prevalence of huge organic structures in the interstellar medium.

Molecules from other galaxies, which were identified by Phil Solomon (Le Tueff *et al.* 2000; table 1), contain a variety of organic molecules, with the largest molecule containing seven atoms, and H_{20} , NH_3 , SO and SiO were also identified. The ubiquity of carbon-based molecules in the interstellar medium and, in particular, from other galaxies provides a tentative empirical indication that carbon-based chemistry may dominate over silicon-based chemistry. However, it should be borne in mind that carbon is a much more abundant element than silicon. Furthermore, most silicon

Table 1. Molecules in other galaxies. (Adopted from Phil Solomon (Le Tueff *et al.* 2000).)

CO	HCN	HNC	CH	CN
NH ₃	HCO ⁺	N ₂ H ⁺	C ₃ H ₂	
CH ₃ OH	C ₂ H	OCS	H ₂ CO	
OH	H ₂ O	SiO	SO	
HCCCN	HNCO	CH ₃ CCH	CH ₃ CN	

compounds, which have a much lower condensation temperature than the corresponding carbon compounds, will be trapped as condensates in dust and will not be easily amenable to identification as free-flying molecules. The open issue of carbon-based chemistry versus silicon-based chemistry in other galaxies is of considerable relevance for astrobiology (Chyba & Hand 2005).

5. IMPACT EVENTS

Reactive processes of asteroid and comet impacts on Earth involve planet–planetary body collisions with impact velocities of tens of kilometres per second. For example, the Shoemaker–Levy comet crashed into Jupiter on 22 July 1994 at a velocity of 60 km s^{−1} (www.jpl.nasa.gov/slg/). Such impact events on Earth generate high temperatures (10⁴–10⁵ K) and pressures (hundreds of kilobars), both in the terrestrial impact region and within the colliding planetary body. Three classes of reactive processes are relevant in this context.

- (i) *Formation of impact craters.* Asteroid and comet impact events constitute the extraterrestrial mechanism, which delivers a localized high-temperature and high-pressure pulse of energy into the target, resulting in extreme local structural and ecological changes (Cockell & Lee 2002). Impact craters could serve as possible sites for prebiotic chemistry (Cockell 2006).
- (ii) *Local chemical effects in the impact region.* An impactor can create a local environment conducive to the synthesis of reduced carbon compounds by the Fischer–Tropsch type reaction (Mukhin *et al.* 1989; Chyba & Sagan 1992). Impact-induced shock heating of reducing gas mixtures in the early Earth's atmosphere could result in the formation of amino acids (Bar-Nun *et al.* 1970).
- (iii) *Hypervelocity impact phenomena within the impactor.* The high-velocity (10–100 km s^{−1}) impact of asteroids or comets, which initially contain prebiotic materials or building blocks of biomolecules, can result in the synthesis of amino acid oligomers (Bernstein 2006). It was experimentally demonstrated that hypervelocity impacts can oligomerize amino acid monomers (Blank *et al.* 2001) and other large organic molecules (Miruma 1995; Managadze *et al.* 2003). Furthermore, organic compounds

can also survive such hypervelocity impacts (Pierazzo & Chyba 1999), providing favourable conditions for the exogeneous delivery of organic materials on Earth.

The dynamics of impactor–target collision pertains to the chemical physics of matter under extreme conditions. A microscopic physical analogue for macroscopic impact events is provided by high-energy cluster–wall collisions. Such processes are triggered by the acceleration of atomic and molecular cluster ions (containing 10–10⁴ constituents with velocities up to approximately 100 km s^{−1} and kinetic energies up to 100 eV per particle), which collide with a molecular or metal solid surface (Schek *et al.* 1994; Schek & Jortner 1996). Thermal femtosecond dynamics of these high-energy clusters (Schek *et al.* 1994) provide a medium for reactive processes, such as dissociation of diatomics embedded in the colliding cluster (figure 2). More interestingly, these impact phenomena induce novel and isothermic chemical processes, such as the N₂ + O₂ → 2NO reaction of the burning of nitrogen (Raz & Levine 2001), providing a basis for novel chemical reactions. Under these extreme conditions, the cluster matter is subjected to a microshock wave propagation within itself, which produces temperatures up to 4 × 10⁴ K and pressures of 600 kbar within (Ar)_n clusters (*n* = 141, 321, 555; Schek & Jortner 1996), with the pressure–temperature Hugoniot curves for the clusters being qualitatively similar to those in the corresponding bulk matter (Ross *et al.* 1986). These extreme pressure conditions result in an extreme compression of the impacting cluster. For example, I. Schek & J. Jortner (1999, unpublished results) observed that the density of the (H₂)_n cluster can be increased by a numerical factor of approximately 1.7 under pressures of 250 kbar and temperatures of 10⁴ K (figure 3). This increased density of the hydrogen cluster is still too low to produce metallic hydrogen. However, there is a distinct possibility that, in other molecular clusters, an impact-induced extreme compression will produce a metallic phase. In such transient metallic clusters, plasma produced by the high-temperature impact may be operative in relevant molecular syntheses (Managadze *et al.* 2003).

High-energy cluster–wall collisions containing prebiotic materials and simple biotic molecules will provide an interesting hunting ground for the production of building blocks of biomolecules under extreme conditions.

6. THE ORIGIN OF LIFE: BOTTOM-UP APPROACH

The bottom-up approach (scheme 2) rests on the sequential steps, which are as follows.

- (i) Molecular fabrication of the building blocks of biomolecules from simple prebiotic molecules induced by external energy sources (Miller 1953; Miller & Urey 1959; Mason 1992; Wills & Bada 2000). These building blocks of biomolecules are produced and dissolved in the ‘primordial soup’ (Darwin 1871; Oparin 1924), where all subsequent reactions occur.

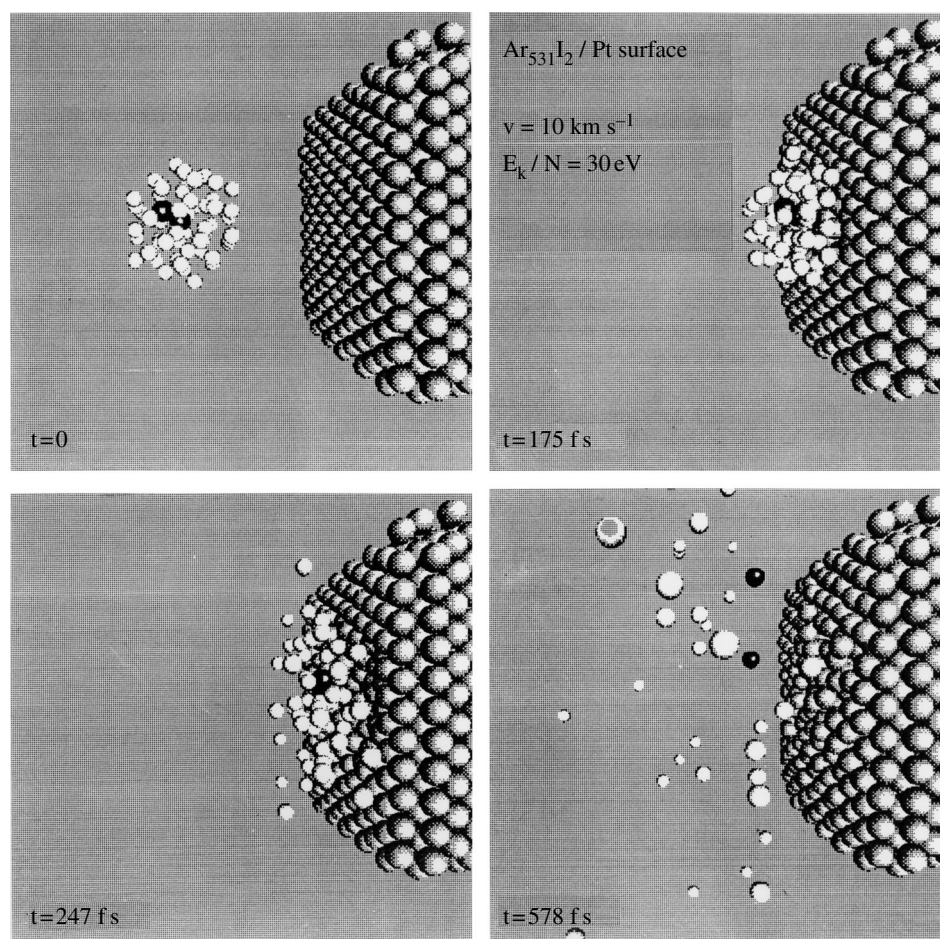


Figure 2. A microscopic physical analogue for impactor–target collisions is provided by high-energy cluster–wall collisions. Reactive chemical dynamics in high-energy Ar_nI_2 cluster–wall collisions are portrayed. Snapshots of the collision of an $\text{Ar}_{531}\text{I}_2$ cluster at an initial velocity of 10 km s^{-1} (kinetic energy of 30 eV per particle) with a platinum surface, as obtained from molecular dynamics simulations, are shown. The dissociation of I_2 is manifested. Data were adopted from [Schek *et al.* \(1994\)](#). High-energy wall collisions of clusters containing prebiotic material or biotic molecules can provide a unique chemical medium for the shock-impact synthesis of building blocks of biomolecules or amino acid oligomers.

the selective catalysis, which maintains the required sequence and regioselectivity of the oligomers ([Ferris 2006](#)). Selective catalysis accomplishes self-organization with the generation of supramolecular diversity, giving access to an array of similar structures that potentially exist ([Lehn 2002a,b](#)). These similar structures correspond to quasispecies ([Eigen 1988](#)). On the other hand, specific catalysis is expected to give rise to a single species, not allowing for the required diversity.

8. THE ROLE OF HUGE NUMBERS

The prebiotic synthesis of proteins or nucleic acids requires the production of an ordered biopolymer. Combinatory arguments reveal that the probability of the formation of compositionally and conformationally ordered systems is negligibly small, in view of the existence of huge numbers of compositional/conformational isomers. These huge numbers of alternative, redundant isomers or conformers constitute a major problem in the description of the evolution of life on Earth ([Levinthal 1969](#); [Joyce & Orgel 1999](#)). Two paradoxes of huge numbers are as follows.

- (i) *The paradox of compositional redundancy* ([Crick 1981](#); [Joyce & Orgel 1999](#)). For a polypeptide

chain containing N amino acids with 20 distinct possibilities for each biological amino acid residue, the total number of structural isomers, $\text{SI} = 20^N$, is huge. Thus, for $N = 200$, $\text{SI} = 10^{260}$! Recent studies on the origin of life focused on RNA as the most important polymer in the early form of life (§9). The same difficulty in the formation of a huge number of isomers has been addressed in the prebiotic synthesis of RNA ([Szostak & Ellington 1993](#); [Joyce & Orgel 1999](#)). An RNA of sufficient length to initiate a high-fidelity catalysis and replication should contain about 40 monomer units. A minimal precondition for the origin of life is two such RNAs catalysing the synthesis of each other. Random polymerization of two RNAs, each containing 40 nucleotides, would result in 10^{48} isomers, weighing 10^{28} g , which is comparable to the mass of the Earth ([Joyce & Orgel 1999](#)). A possible resolution of this paradox of structural redundancy rests on the role of self-organization by design and selection ([Eigen 1971, 1996](#); [Lehn 2002a,b, 2003](#); [Heckl 2004](#); [Ferris 2006](#); [Deamer 2006](#)), which may be driven by selective catalysis ([Ferris 2006](#)), as discussed in §7.

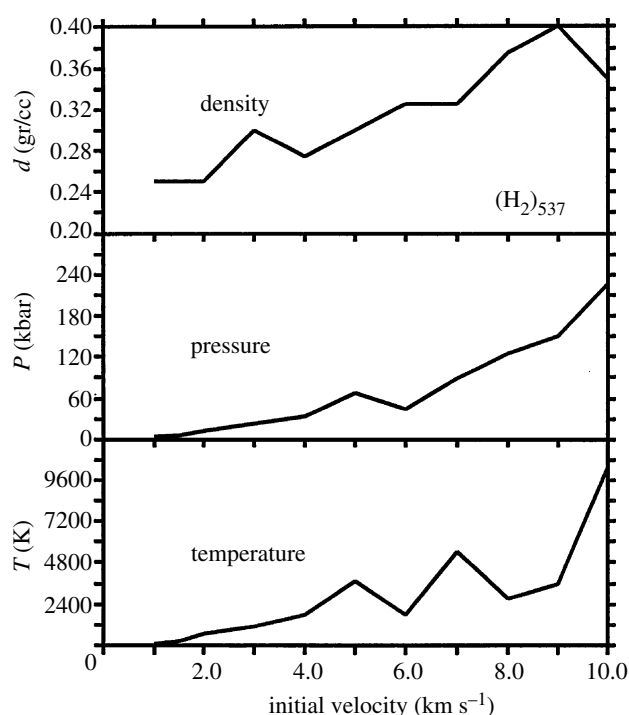


Figure 3. Microscopic modelling of matter under extreme conditions created by high-energy impactor–target collisions, portraying microshock wave propagation producing high temperatures and pressures in high-energy $(\text{H}_2)_{537}$ clusters colliding at velocities of 1–10 km s^{-1} with a platinum wall (I. Schek & J. Jortner 1999, unpublished results). High densities (up to a numerical factor of 1.7 of the normal density), high temperatures (up to 10^4 K) and high pressures (up to 250 kbar) are generated, providing a unique medium for the production of building blocks of biomolecules under extreme conditions.

- (ii) *The paradox of conformational redundancy* (Levinthal 1969). Protein folding describes the complex process in which polypeptide chains adopt their three-dimensional native conformation required for their biological function. Levinthal (1969) pointed out that for a protein made up of 100 amino acids, with three possible conformations for each amino acid residue, there are 3^{100} (approx. 10^{49}) conformations for the entire polypeptide chain. Even if the time required to change from one configuration to another is only 10 ps, a random search through all the conformation spaces will require 10^{36} s or 10^{29} years. The Levinthal (1969) paradox implies that protein folding would take longer time than the age of the universe! The Levinthal argument is based on the unphysical assumption that the energy landscape (potential energy surface) of the protein corresponds to a ‘golf course’, being totally flat with one hole for the native configuration (figure 4), and with all configurations of equal probability (Zwanzig *et al.* 1992). In real life, the energy landscape of a polypeptide or protein (figure 4) is rugged with a very large number of minima, basins (‘valleys’) and saddle points (‘mountain ridges’). The system slides from the initial configuration on the energy landscape to the global minimum. The energy landscapes of proteins govern both folding kinetics and

thermodynamics (Berry 1993; Fraunfelder & Wolynes 1994; Wolynes *et al.* 1995).

From the foregoing discussion, indications emerge regarding the central role of self-organization and dynamics on energy landscapes in overcoming compositional and conformational redundancy in the prebiotic synthesis of proteins and nucleic acids.

9. THE ORIGIN OF LIFE: TOP-DOWN APPROACH

Self-organization, which plays a central role in the construction of complex matter, supplements the bottom-up molecular fabrication in terms of top-down miniaturization (Lehn 2003). The top-down approach to the origin of life rests on two major aspects, which are as follows.

- (i) *Deconstructuralism of a system to small units that still exhibit biological functions.* A great success of this approach pertains to the discovery that the RNA molecule is capable of both catalytic activity and information storage (Altman *et al.* 1989; Cech 1993). This provided a solution to the puzzle (Dyson 1985) whether proteins preceded DNA or vice versa. In an ‘RNA world’, the RNA molecule performs the dual function of both present-day proteins that act as enzymes to catalyse reactions and DNA that acts to store molecular information (Crick 1968; Orgel 1968, 1988a,b, 2000; Orgel & Lohrman 1974; Cech *et al.* 1981; Gilbert 1986; Joyce & Orgel 1999; Taylor 2006). A major problem in this attractive picture is that the prebiotic origin of RNA remains mysterious (Shapiro 1988; Chyba & McDonald 1995; James & Ellington 1995).
- (ii) *Mapping the genetic relationship of life on Earth to elucidate the properties of the last common ancestor* (Hutchison *et al.* 1999; Marshall 2002). At the level of the complete cell, efforts are now made to strip down a genome to reveal the minimal set of genes required for cellular functionality (Hutchison *et al.* 1999; Marshall 2002).

10. SOME OPEN QUESTIONS

The foregoing discussion already reflected on the ubiquity of open questions, starting from the current absence of a scientific theory for the ‘definition of life’. We then alluded to many gaps in our understanding of the conditions and constraints for prebiotic chemistry. Several open questions in this fascinating field that are of considerable interest are as follows.

- (i) *The origin of biomolecular chirality.* This constitutes an important, extensively discussed and controversial issue (Quack 2002, 2003). It concerns a nearly exclusive selection of L-amino acids and D-saccharides for terrestrial biopolymers. Parity violation of molecular and biomolecular chiralities is important; however, energy differences between chiral molecules are small, being in the range of picojoules per mole (10^{-11} – 10^{-12} J mole $^{-1}$; Quack 2002).

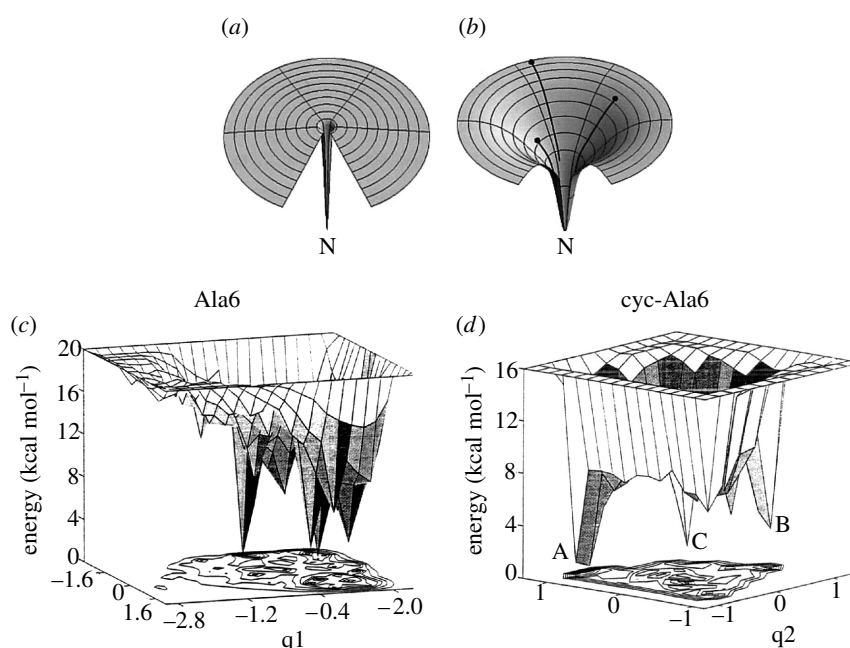


Figure 4. Energy landscapes of complex systems. The energy landscapes of cyclic (alanine)₆ polypeptides were obtained from molecular dynamics simulations. These energy landscapes of (c) linear (Ala6) and (d) cyclic (cyc-Ala6) polypeptides portray the potential energy surfaces in the two reduced coordinates obtained from the principal coordinate analysis (adopted from [Levy *et al.* 2002](#)). The two potential energy surface models show the grossly oversimplified energy landscapes for (a) a golf course, corresponding to the Levinthal picture, and (b) a funnel. Motion on the real energy landscape of a complex system overcomes conformational redundancy, which is only inherent in the oversimplified model (a) for a golf course.

Fundamental hypotheses for the prebiotic enantiomer enrichment involve the following: (i) mechanisms driven by parity violation ([Quack 2002](#)), (ii) homochiral selection by photolysis with circularly polarized light ([Meierhenrich & Thiemann 2004](#)) and (iii) stochastic and accidental mechanisms. The latter rest on the suggestions for low-temperature phase transitions under the influence of parity violation ([Salam 1991](#)) or on a nonlinear kinetic scheme with a very small selective advantage arising from parity violation ([Chela-Flores 1991](#)). Some interesting compound mechanisms for the emergence of homochirality were proposed ([Koch *et al.* 2002](#); [Pizzarello & Weber 2004](#); [Nanita & Cooks 2006](#)). These involve a sequential-parallel scheme of chiral imbalance (presumably arising from parity violations ([Quack 2002, 2003](#)) or photolytic selection ([Meierhenrich & Thiemann 2004](#))), followed by chiral enrichment (presumably driven by chiral synthesis; [Pizzarello & Weber 2004](#)) and, subsequently, chirality transfer. One possible process for chirality transfer involves homochirality preference by an enantiometric substitution of individual amino acids or sugars on (serine)₈ H⁺ ‘magic number’ clusters ([Julian *et al.* 2002](#); [Nanita & Cooks 2006](#)). Not only is the homochirality problem unsolved, but also it is intriguing to inquire whether primitive life was homochiral. Notable, but rare, cases of the violation of homochirality in living matter involves the presence of D-amino acids in some bacteria ([Foster & Popham 2002](#)) and in some

antibiotics produced by bacteria ([Lenler *et al.* 1999](#)). D-Glutamic acid is the prominent enantiomer incorporated into poly- γ -glutamic acid in the capsules of *Bacillus subtilis* and some other bacteria ([Foster & Popham 2002](#)). The ratio of D- and L-glutamic acid residues in poly- γ -glutamic acid can vary, depending on the rate of the production of D-glutamic acid in the cell ([Ashiuchi *et al.* 1999](#)). D-Alanine residues in the bacterial cell wall of *Staphylococcus aureus*, a Gram-positive organism, are involved in antibiotic resistance ([Sieradzki & Torrias 2006](#)). One of the best-studied peptide antibiotics, from the biosynthetic point of view, is gramicidin S, which contains D-phenylalanine ([Lenler *et al.* 1999](#)). Accordingly, D-glutamic acid, D-alanine, and D-phenylalanine exist in biologically active peptide chains of bacteria, making them resistant to proteolytic enzymes ([Sieradzki & Torrias 2006](#), [Cui *et al.* 2006](#)). At present, the experimental and theoretical basis for a proper mechanism of homochirality requires further scrutiny and the problem is open.

- (ii) *The build-up hierarchy.* The understanding of bottom-up self-organization requires an experimental control of molecular fabrication and biomolecular non-fabrication in model systems. In particular, the mechanistic facets of the ‘holistic’ (‘collective’) one-step (or few steps) self-organization of the building blocks of biomolecules to form complex biomolecules have to be elucidated. Concurrently, the advancement of theoretical concepts, which can be subjected to experimental tests, is imperative.

- (iii) *The top-down approach to the origin of life.* Some of the important open questions are related to the understanding of the prebiotic origin of RNA and the elucidation of the properties of the last common genetic ancestor. The latter issue can give rise to the first artificial genome (Hutchison *et al.* 1999; Marshall 2002), opening up avenues towards ‘artificial life’.
- (iv) *The organization and function of complex biological matter.* This constitutes one of the central ‘grand questions’ of modern science. For the sake of methodology, we follow Lehn (2003) adopting a constructionalist approach, noting that the organization of complex biological matter is induced by electromagnetic forces. Molecular recognition, which is based on such interactions, provides a central cause for self-organization at the molecular, supramolecular and nanostructural level. The second, related but distinct, ‘grand question’ addresses the cosmological organization of matter by gravitational forces (Lehn 2003). Some of the many fascinating open questions in the realm of complex biological matter are as follows. (i) What are the mechanistic aspects of information-driven self-organization? (ii) What is the nature of the ‘transition’ from programmed and instructed systems to learning (and thinking) systems? (iii) What are the complementary roles of bottom-up construction and top-down miniaturization? (iv) At what level of molecular–supramolecular–nanostructural complexities does biological function set in? Perhaps, the most important issue is the complete, unambiguous functional characterization of complex biological matter.
- (v) *Time-scales for the origin of life.* The characteristic time, τ_{OL} , for the onset of the origin of life on Earth (an incompletely defined, but useful concept) must be shorter than two times: the time $\tau_O \approx 4.6$ Gyr for the formation of Earth by terrestrial accretion (Chyba & Hand 2005; Lunine 2006) and the time $\tau_E \approx 4.0$ Gyr for the onset of the appropriate geological, environmental and chemical conditions that enable the emergence of life. τ_E is determined by (at least) three times (that are given relative to the time for the formation of the earth): (i) $t_1 \approx 0.1$ Gyr for the solidification of the magma ocean to form the crust (Solomatov 2000); (ii) $t_2 \approx 0.5$ Gyr for the termination of the heavy impact bombardment (Maher & Stevenson 1988); (iii) $t_3 \approx 0.6$ Gyr for the possible stabilization of surface liquid water (Lunine 2006), while some geological evidence (Watson & Harrison 2005) indicates that $t_3 \approx 0.3$ Gyr. We expect that $\tau_E < (\tau_O - t_1)$ and $\tau_E < (\tau_O - t_2)$, while $\tau_E \leq (\tau_O - t_3)$. As a rough estimate we now take $\tau_E \approx \tau_O - (t_1 + t_2) \approx 4.0$ Gyr. We note in passing that τ_{OL} marks the origin of life, not of intelligent life, with the latter being characterized by a much shorter lifetime of $\tau_{OIL} \approx 10\text{--}50$ Myr (Chyba & Hand 2005). The hierarchy of time-scales is $\tau_O > \tau_E > \tau_{OL} \gg \tau_{OIL}$, with all these times being relative to the present time. Following the extensive review of Chyba & Hand (2005),

estimates of τ_{OL} were inferred from geological and planetological evidences, which gave $\tau_{OL} = 3.5$ Gyr, while stable isotope chemistry yielded $\tau_{OL} \approx 3.8\text{--}3.9$ Gyr. Thus, life appeared on the early Earth at the time-scale of $\tau_O - \tau_{OL} \approx 0.7\text{--}1.1$ Gyr of its formation, according to the ‘central dogma’ underlying this discussion meeting. The time window $\Delta t = \tau_E - \tau_{OL}$ marks the time-scale for the evolution of primitive life on the early Earth, which falls in the range $\Delta t \approx 0.1\text{--}0.5$ Gyr. This timing is important for the qualitative assessment of the nature of the chemical processes that led to the formation of complex biological material on the early Earth. For $\Delta t \approx 0.1$ Gyr, the formation of life was ‘easy’, while for $\Delta t \approx 0.5$ Gyr, the formation of life was ‘hard’ (Chyba & Hand 2005). The distinction between the ‘hard’ and the ‘easy’ formation of early life can be highlighted by the adaptation of the Carter formula (Carter 1983; Barrow & Tiepler 1988) and its slight extension (Jortner 2006, unpublished results). Provided that the onset of early life involved n improbable and independent steps, then $\Delta t/\tau_E = \beta n/(\beta n + 1)$, and $\tau_{OL}/\tau_E = 1/(\beta n + 1)$, where β ($\beta \ll 1$) is a dynamic time-stretching parameter (Jortner 2006, unpublished results). ‘Short’ time windows, e.g., $\Delta t \approx 0.1$ Gyr with $\tau_{OL}/\tau_E \approx 0.98$ imply that $n\beta$ and n are negligibly small (manifesting the ‘easy way’), while ‘long’ time windows, e.g., $\Delta t \approx 0.5$ Gyr with $\tau_{OL}/\tau_E = 0.88$ imply that $n\beta \approx 0.12$, so that $n \approx 1\text{--}2$ (manifesting the ‘hard way’).

The fascinating scientific work reported at this discussion meeting reflects on the quest for front-line solid experimental evidence and theoretical understanding, which will provide the conceptual basis for the understanding of the emergence of life on the early Earth.

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